

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in or relating to the Modification and Production of Titanium Ester Compounds

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of chemically modifying titanium esters and more particularly to a method of ester exchange whereby new and useful titanium esters may be obtained.

The formation of tetraalkyl titanates (also known as ortho esters of titanium), through direct reaction of the alcohols with titanium tetrachloride in the presence of ammonia, is well known. Such a process is disclosed in Specifications Nos. 479,470 and 512,452. The exchange of the organic radicals of titanium esters through alcoholysis is set forth in the literature. However, for the preparation of some esters neither of these methods is suitable.

It is an object of the present invention to provide a process of chemically modifying titanium esters whereby titanium esters are obtained different from the starting esters.

According to the present invention, there is provided a process for chemically modifying a tetra or mixed orthotitanate of the formula  $Ti(OR)_4$ , or a polymeric titanate of the formula  $RO[-Ti(OR)_2O-]_xR$ , wherein R is an alkyl aryl, aralkyl or cycloalkyl radical and x is an integer greater than 1, which comprises transesterifying such a titanium ester with a carboxylic acid ester containing at least one organic radical in its alcohol-derived portion which is different from at least one organic radical of the titanium ester and containing no free hydroxyl groups, to form a

product titanium ester different from the reactant titanium ester and a co-product carboxylic acid ester different from the reactant carboxylic acid ester.

The polymeric titanium esters of the formula  $RO[-Ti(OR)_2O-]_xR$  referred to above may be prepared from the corresponding orthoesters by reaction with water and subsequent condensation. The orthotitanates or orthoesters are sometimes referred to as titanium alcoholates and phenolates.

Where it is desired to replace all four ester groups of a titanium orthoester starting metal with ester groups derived from the carboxylic acid ester, approximately four moles of the latter are preferably employed per mole of titanium orthoester. Similarly where it is desired to replace only two ester groups, approximately two moles of the carboxylic acid ester are employed per mole of titanium orthoester. Where it is convenient, the reaction products are desirably separated, preferably as they are formed, for example by distillation.

In a preferred embodiment the invention comprises bringing together a titanium ester of the formula  $Ti(OR)_4$ , R being an alkyl, aryl, aralkyl, or cycloalkyl radical of carbon atom content of at least 6, as for example tetraoctyl titanate, with a carboxylic acid ester of a polybasic alcohol, as for example coconut oil, in stoichiometric proportion to form a stable intermediate solution, heating said solution to effect transesterification between the tetraoctyl titanate and the coconut oil, forming a solid tough body of glycerol, monoglyceride and diglyceride titanates plasticized by the octyl esters of the coconut acids. The heat is conveniently applied by radiation, but also may be done by baking, or other suitable means. Temperatures within the range of 50° C. to 200° C. are suitable in effecting the metathetical reaction.

To a clearer understanding of the invention, the following specific examples are given. These examples are merely in illustration, but not in limitation of the invention:

EXAMPLE I.

Four hundred sixty four parts by weight of *n*-butyl acetate were added with agitation to 284 parts of tetraisopropyl titanate in a reaction vessel. The reaction mixture was heated and the co-product isopropyl acetate was removed by fractional distillation, the temperature being raised to 90° C. The residual product was tetra-*n*-butyl titanate.

EXAMPLE II.

Two hundred thirty two parts by weight of *n*-butyl acetate was added with agitation to 284 parts of tetraisopropyl titanate in a reaction vessel. The reaction was heated, and the co-product isopropyl acetate was removed by fractional distillation, the temperature being raised to 90° C. The residual product was diisopropyl di-*n*-butyl titanate.

EXAMPLE III.

To 166 parts by weight of guaiacol acetate was added a solution of 142 parts by weight of tetraisopropyl titanate in 306 parts by weight of xylene, the mixture placed in a fractionating still and 101.5 parts by weight (equivalent to 99.5% theoretical) of isopropyl acetate, boiling at 88° C. was removed. The xylene was separated from the still residue by vacuum distillation leaving the product diguaiacol diisopropyl titanate.

EXAMPLE IV.

Four mole parts by weight of phenyl benzoate and one mole part by weight of tetraisopropyl titanate were mixed in a vacuum distillation apparatus. During distillation, the theoretical amount (4 mole parts by weight) of isopropyl benzoate was removed at about 40 mm. pressure. The resulting orange-red crystalline product was tetraphenyl titanate.

EXAMPLE V.

33.8 parts by weight of coconut oil and 18.6 parts by weight of tetraoctyl titanate were comixed. The mixture was spread as a thin film on a glass slide and baked at 170° C., at which temperature the liquid film set up and became a solid clear plastic composition in the form of a film. Interaction took place during the baking to give a new durable plastic product, suggesting its use as a plastic film and as an ingredient in coating compositions.

EXAMPLE VI.

Thirty parts by weight of a pentaerythritol phthalate resin completely esterified with soya bean acid were mixed with 5 parts by weight of tetrastearyl titanate dissolved in 24 parts by weight of xylene. The solution so obtained was flowed onto a glass slide to form a thin sheeted film and heated to approximately 120° C. under an infrared lamp. The resulting product was harder and more abrasion resistant than a film of the unmodified glyptal resin similarly prepared. During the heat treat-

ment reaction took place between the resin ester and the titanium ester. The heat also caused evaporation of the volatiles from the product.

EXAMPLE VII.

Thirty parts by weight of a commercial resin solution product sold under the trade name "Syntex" 120 (Registered Trade Mark) (an epichlorohydrin-bis-phenol copolymer completely esterified with soy acids) were mixed with three parts by weight of tetrastearyl titanate dissolved in 15 parts by weight of xylene. The solution obtained was spread onto a glass surface and heated as in the preceding example under an infra-red lamp to approximately 120° C. The resulting sheeted plastic product was more resistant to xylene than was the original Syntex 120 heated similarly. The above-prepared solution of Syntex 120 and tetrastearyl titanate could be gelled by heating to approximately 70° C. showing metathetical reaction between the two esters at this temperature.

In the foregoing Examples V, VI and VII, the formation of a product titanium ester different from the initial titanium ester cannot be directly demonstrated as the products of the reaction are not separated. To take the case of Example V, for example, the occurrence of the reaction according to the invention may be inferred from the following considerations. Coconut oil alone will not form a durable plastic film on heating and, since it contains substantially no free hydroxyl groups which could react with the titanium ester by simple substitution, one is led to the conclusion that the formation of a plastic film indicates that ester interchange between the initial titanium ester and the coconut oil has taken place. Similar considerations apply to Examples VI and VII.

EXAMPLE VIII.

568 grams of tetraisopropyl titanate were placed in a dry flask fitted with a distillation column and an agitator. A solution of 18 grams of water in 200 grams of isopropanol was added slowly with agitation. Upon distillation of the isopropyl alcohol a residue of approximately one mol of hexaisopropyl dititanate was left as a product of the partial hydrolysis of the initial isopropyl titanate. A solution of benzyl acetate dissolved in 250 grams of normal octane was then added to this residue and agitated. The mixture was then distilled under reflux conditions and 200 grams or approximately 2 mols of isopropyl acetate were recovered in the distillate. The octane solvent was then distilled from the contents of the flask leaving as a residue about 500 grams of a titanium ester containing 31% TiO<sub>2</sub>. From this analysis, the weight of the final product and the amount of isopropyl acetate recovered, the product is indicated to be tetraisopropyl dibenzylidititanate.

As stated above, titanium esters utilizable

within the scope of the invention include tetra and mixed orthotitanates of the formula  $Ti(OR)_4$  and condensed or polymeric titanates of the formula  $RO[-Ti(OR)_2O-]_xR$ , where in R is an alkyl, aryl, aralkyl or cycloalkyl radical and x is an integer greater than one. Alkyl radicals of eight carbon chain length or less are preferred, in reactions where it is desired to separate the reaction products by distillation. In reactions where it is desired to allow the reaction products to remain together without separation, higher chain length, or the higher-molecular-weight alkyl or aryl groups are useful. The carboxylic ester reaction product in some applications can be usefully allowed to remain in admixture with the newly formed titanium ester as a modifier of the plastic product as shown in Example VII.

Specific titanium esters suitable for use in the process of the invention include tetra-alkyl titanates such as tetraethyl titanate, tetra-n-propyl titanate, tetraisopropyl titanate and tetrastearyl titanate; tetraaryl titanates such as tetraphenyl titanate; mixed alkyl titanates such as dimethyl diisopropyl titanate, diethyl distearyl titanate, diisopropyl diphenyl titanate and diethyl dicyclohexyl titanate; polymeric or condensed alkyl or aryl titanates, such as polyisopropyl titanate, polyisoamyl titanate, and polyphenyl titanate, and substituted alkyl and aryl titanates, such as tetra-monochloroethyl titanate, and tetra-dichlorophenyl titanate.

The carboxylic acid esters which may be employed in this invention include any organic compound containing the ester linkage

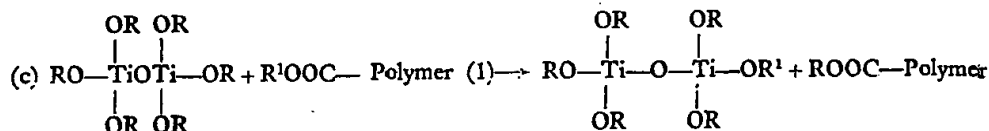
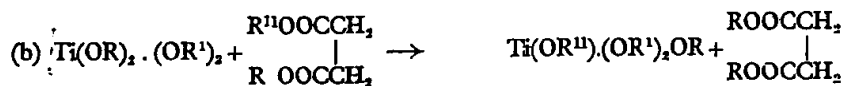


indicated by the structure, where A is hydrogen or the carbon atom,  $\equiv C$ , of an organic group. Thus, the simple esters of the type  $R_2CCOOCR$ , where R is hydrogen or a hydrocarbon radical as well as the poly-esters containing chains of ester linkages, can be used, as can multiple esters other than those usually referred to as polyesters, such as the esterification products of di, tri and polybasic acids with mono, di and polyhydroxy alcohols, and the esterification products of di, tri and polyhydroxy alcohols with monobasic acids. The hydrocarbon radicals present in the esters may be alkyl, cycloalkyl, aryl, cycloaryl and of mixed hydrocarbon

structure. Furthermore, the presence of compatible substituents such as ether groups or chloro-hydrocarbon radicals in the R groups is also a possible characteristic of the organic esters useful in this invention. Examples of these radicals are  $CH_3-$ ,  $C_2H_5-$ ,  $CH_2=CHCH_2-$ ,  $C_6H_5-$ ,  $CH_2C_6H_4-$ ,  $C_6H_{11}-$ ,  $C_6H_5CH_2-$ ,  $-CH_2-CH_2-$ ,  $-C_6H_4-$ ,  $C_6H_4Cl-$ ,  $CH_3-O-C_6H_4-$ , and  $-CH_2-C\equiv$ . Since these radicals are to be substituted for those in the titanium esters the types suitable for one reactant find use in the other reactant. It is also possible to use organic esters of dibasic carboxylic acids as well as carboxylic acid esters of polybasic alcohols. The selection of the carboxylic acid ester for a particular operation will depend on the desired reaction product and separation of the co-products when the latter is to be effected.

Among the specific carboxylic acid esters which may be used within the scope of the invention are included those formed by reaction of monohydric alcohols with monobasic carboxylic acids of which n-butyl acetate, isobutyl acetate, isoamyl acetate, ethyl benzoate, and n-amyl stearate are examples; those formed by the reaction of polyhydric alcohols with monobasic carboxylic acids, of which glycerol triacetate, glycol diacetate, propylene glycol diacetate, and glycerides as in naturally occurring oils and fats, are examples; those formed by the reaction of polyalcohols and polybasic carboxylic acids of which the glycerol-phthalic acid polyesters and ethylene glycol-phthalic acid polyesters are examples; those formed from monohydric alcohols and polybasic carboxylic acids, of which the dimethyl sebacate and polymethylmethacrylate are examples, and fatty acid esters of co-polymers, an example of which is the soy acids esters of "Epon" resin, "Epon" resin being a co-polymer of epichlorhydrin and p, p'-biphenol.

The transesterification reaction of the invention may be illustrated by the following equations, wherein a titanium ester is reacted with an organic ester, said organic ester reactant having at least one organic radical derived from the alcohol portion of the organic ester which is different from at least one of the organic radicals of the titanium ester reactant.



(1) such as polymethacrylate, where R, R<sup>1</sup> and R<sup>11</sup> are all different and are alkyl, aryl, aralkyl or cycloalkyl radicals.

A solvent for the reactants or reaction mixture is sometimes found to be advantageous. Usually, an anhydrous hydrocarbon solvent is preferred, but any inert anhydrous organic solvent may be used.

The reactions of this invention can take place under varying conditions but mild application of heat is generally desired as the metathesis is favored by rise in temperature. The liquid state for both ester reagents is also advantageous and this condition is realized in an undiluted system when the reactants are liquids, at normal temperatures. When one or both of the esters are solids, the liquid state may be reached by an elevation of temperature or by the use of solvents as disclosed above. Temperatures of from 50° C. to 200° C. may be selected but a temperature within the range of 75° C. and 125° C. is considered as giving good results within a reasonable reaction time.

The production of new and useful titanium esters of known composition is possible by our process as it has been disclosed when using the esters having the hydrocarbon radicals enumerated above. There is no tendency to unduly complicated chemical reactions when the saturated aliphatic radicals as listed earlier in this specification are used in these metathetical reactions.

The advantages of the invention include not only an improved method for the preparation of titanium esters difficult to prepare by older methods, but also include an alternate method for the preparation of those carboxylic acid ester co-products not easily or economically prepared by the usual methods of manufacturing such organic esters.

What we claim is:—

1. A process for chemically modifying a tetra or mixed orthotitanate of the formula Ti(OR)<sub>4</sub> or a polymeric titanate of the formula RO[—Ti(OR)<sub>2</sub>O—]<sub>x</sub>R, wherein R is an alkyl, aryl, aralkyl or cycloalkyl radical and x is an integer greater than 1, which comprises transesterifying such a titanium ester with a carboxylic acid ester containing at least one organic radical in its alcohol-derived portion which is different from at least one organic radical of the titanium ester and containing no free hydroxyl groups, to form a

product titanium ester different from the reactant titanium ester and a co-product carboxylic acid ester different from the reactant carboxylic acid ester.

2. A process according to Claim 1, wherein the substituents R each contain at least 6 carbon atoms.

3. A process according to Claim 1, wherein said titanium ester is tetraisopropyl titanate and said carboxylic acid ester is n-butyl acetate.

4. A process according to Claim 3, wherein the tetraisopropyl titanate and the n-butyl acetate are employed in approximately stoichiometric quantities.

5. A process according to Claim 3 wherein the tetraisopropyl titanate and the n-butyl acetate are employed in the proportion of approximately one mole of the former per two moles of the latter.

6. A process according to Claim 1, wherein said titanium ester is tetraisopropyl titanate and said carboxylic acid ester is guaiacol acetate, the tetraisopropyl titanate and the guaiacol acetate being employed in the proportion of approximately one mole of the former per two moles of the latter.

7. A process according to any of the preceding Claims including the step of separating the reaction products.

8. A process according to Claim 7, wherein the reaction products are separated as formed, for example, by distillation.

9. A process according to Claim 2 wherein the carboxylic acid ester is an ester of a polyhydroxy organic compound.

10. A process according to Claim 9, wherein the reaction mixture is heated to a temperature above its gel point and the products of the reaction are not separated.

11. A process according to either of Claims 9 or 10, wherein the titanium ester is tetraoctyl titanate and the carboxylic acid ester is coconut oil.

12. A process for chemically modifying a titanium ester substantially as herein described with reference to the examples.

13. Modified titanium esters when produced by the process according to any of the preceding claims.

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